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Sorption of ofloxacin and chrysoidine by grape stalk. A representative case of biomass removal of emerging pollutants from wastewater



Valeria M. Nurchi ^{a,*}, Miriam Crespo-Alonso ^a, Maria I. Pilo ^b, Nadia Spano ^b, Gavino Sanna ^b, Rosanna Toniolo ^c

^a Dipartimento di Scienze Chimiche e Geologiche, University of Cagliari, Cittadella Universitaria, 09042 Monserrato, Cagliari, Italy

^b Dipartimento di Chimica e Farmacia, University of Sassari, via Vienna 2, 07100 Sassari, Italy

^c Dipartimento di Scienze e Tecnologie Chimiche, University of Udine, via Cotonificio 108, 33100 Udine, Italy

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Abstract Emerging pollutants, as antibiotics or dyes, in aquatic ecosystems are a crucial concern and numerous techniques have been developed for their removal. Efficiency, cost effectiveness, and biodegradability reveal biomass sorption as one of the most appealing methods. This study aims to evaluate the effectiveness of grape stalk as a sorbent for ofloxacin (a fluoroquinolone antibiotic) and chrysoidine (an azo-dye). The kinetic and the thermodynamic aspects of the sorption were studied. A pseudo first-order kinetic behavior is shown by both substances, though the kinetic constants of ofloxacin are almost double than those of chrysoidine. The sorption isotherms, which strictly follow the Langmuir model, show remarkable differences as a function of pH and of biomass size. The trend of Langmuir parameters, Q_{\max} and K , as a function of pH and size, is discussed, and different binding mechanisms are proposed. Kinetic and thermodynamic parameters prefigure grape stalk as a potential biomass for scavenging toxic substances from wastewater.

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1. Introduction

Various organic compounds of different origin strongly contribute to the pollution of urban, industrial and agricultural wastewater. Pharmaceuticals, illicit drugs, hormones and steroids are diffused pollutants in urban water and in effluents from animal farms (Crespo-Alonso et al., 2013). Azo-dyes, widely used in leather, rubber, textile and food industries, constitute a significant class of industrial pollutants: colored effluents, besides their unpleasant impact on the environment, are critical for their toxicity toward aquatic organisms (Nurchi

* Corresponding author. Tel.: +39 070 675 4476; fax: +39 070 675 4478.

E-mail address: nurchi@unica.it (V.M. Nurchi).

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et al., 2014). The removal of these classes of pollutants is thus an impelling environmental issue. Among the numerous techniques used to this end, sorption has been found an effective method for scavenging organic pollutants from wastewater, and activated carbon is surely the most valuable sorbent thanks to its high sorption capacity, though its relatively high cost limits large-scale applications. Recent reviews pointed out that sorption by biomass, besides being an effective method for removing pollutants, presents further advantages related to efficiency and simplicity of use, but, above all, to cost-effectiveness and biodegradability (Nurchi and Villaescusa, 2008, 2012; Nurchi et al., 2010; Guiso et al., 2012). Lately, we studied the ability of row cork, a strong sorbent of polluting heavy metal ions (Villaescusa et al., 2002; Nurchi et al., 2008; Dordio et al., 2011), to remove (R)-9-fluoro-3-methyl-10-(4-methylpiperazin-1-yl)-7-oxo-3,7-dihydro-2H-[1,4]oxazino[2,3,4-ij]quinoline-6-carboxylic acid (ofloxacin) (Crespo-Alonso et al., 2013) and 1,3-benzenediamine-4-(phenylazo)-monohydrochloride (chrysoidine) (Nurchi et al., 2014), a synthetic azo-dye widely used in the textile industry (Lei et al., 2011), from aqueous solutions (Scheme 1).

These studies, mainly based on equilibrium isotherms, rationalized the results at different pH values on the basis of the pH-dependent behavior of the biomass (point zero charge, PZC) and of the sorbates, whose acido-base properties were thoroughly examined by potentiometric and spectrophotometric measurements. The results with cork encouraged us to extend our studies to a different biomass, grape stalk, largely available as a residue of wine-making activities. It was widely studied for the removal of toxic metal ions from aqueous systems by Zoubolis et al., 2002 for copper, zinc, and nickel, by the group of Villaescusa for chromium (Fiol et al., 2003; Escudero et al., 2006, 2017; Fiol et al., 2008), copper and nickel (Villaescusa et al., 2004; Escudero et al., 2013b), and lead and cadmium (Martinez et al., 2008; Miralles et al., 2010). Recently grape-stalk residues have been also studied for paracetamol sorption (Villaescusa et al., 2011).

Grape stalk composition, cellulose (30.3%), hemicellulose (21.0%), lignin (17.4%), tannins (15.9%), proteins (6.1%) and ash, (7.0%) (Prozil et al., 2012), remarkably differs from that of cork, suberin (40%), lignin (22%), cellulose and hemicellulose (20%), being waxes, tannins, and other extractable compounds of the remainder (Villaescusa et al., 2002). Also the PZC value of grape stalk (5.0) differs from that of row cork (3.6) (Fiol and Villaescusa, 2009). The composition and PZC of grape stalk could reasonably extend the sorption

pH interval with characteristics better than cork. We use ofloxacin and chrysoidine as models of antibiotic and dye pollutants taking advantage of the previous detailed characterization of the acido-base properties (Crespo-Alonso et al., 2013; Nurchi et al., 2014).

2. Materials and methods

2.1. Materials

All the reagents (ofloxacin, chrysoidine, KOH, KCl and HCl), purchased from Aldrich (analytical grade), were used without further purification. Ofloxacin and chrysoidine stock solutions were prepared by dissolving the proper amount of each compound in double-distilled water, being both easily soluble in water (ofloxacin 28 mg/mL, 77 mM; chrysoidine 20 mg/mL, 80 mM).

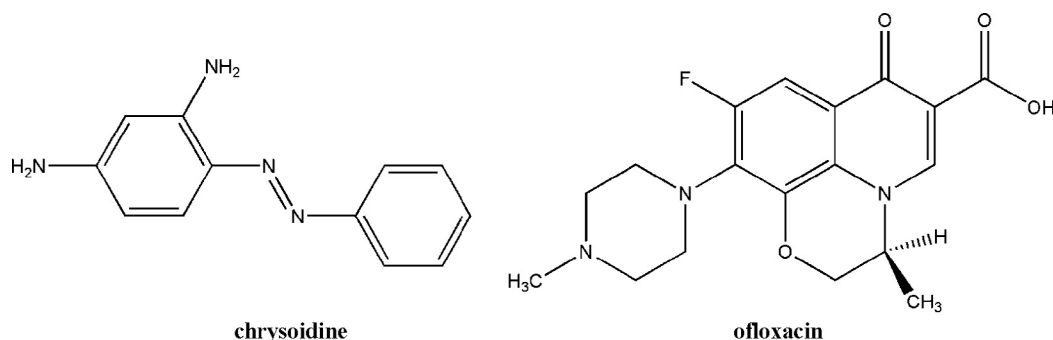
Buffer solutions 0.05 M were prepared from potassium hydrogen-phthalate/HCl (pH 4), potassium dihydrogen-phosphate/KOH (pH 7), and sodium tetraborate/HCl (pH 9).

Grape stalk wastes, supplied by a Sardinian wine producer, were washed with distilled water three times, dried at 60 °C in an oven under vacuum till constant weight, and then cut. Samples of two different sizes were selected by sieving, the first one (FG) ranging from 35 to 60 mesh and the second one (GG) from 10 to 16 mesh.

2.2. Kinetic studies

Five sets (three for ofloxacin at pH values 4, 7 and 9; two for chrysoidine at pH 4 and 7) of 12 tubes were prepared to assess the equilibration time with FG grape stalk. The three pH values for ofloxacin are those where each of the three species, LH_2^+ (pH 4), LH (pH 7), and L^- (pH 9), is the predominant one (Crespo-Alonso et al., 2013); the two pH values for chrysoidine were chosen on the same basis, taking into account the existence of the two species LH^+ (pH 4), and L (pH 7) (Nurchi et al., 2014). A constant amount of biomass (0.5 g, exactly weighed using a 4-digit analytical balance) was put in contact with 40 mL of chrysoidine or ofloxacin solutions of given concentrations (3.1 mM or 7.0 mM, respectively), according to the sorption procedure reported in the following section.

Equilibrium concentrations of chrysoidine or ofloxacin were determined at different contact times. Kinetic trends were obtained by plotting the sorbed substance per unitary weight of biomass values (Q) vs the contact time t .



Scheme 1 Chemical structure of chrysoidine a) and ofloxacin b).

2.3. Sorption isotherm procedure

Sorption isotherms were determined by batch equilibrium sorption procedures. An amount of biomass of about 0.5 g, exactly weighed using a 4-digit analytical balance, was added to a set of 40 mL ofloxacin solutions (ofloxacin concentrations spanned from 0.5 mM to ~7 mM) at buffered pH values (4, 7, and 9) in a series of Falcon™ tubes. The mixture was allowed to equilibrate overnight on a tube rotator (Falc F200 at constant speed 9 rpm). Each sorption isotherm was covered with at least 11 points, i.e. 11 solutions of increasing ofloxacin concentration. The sorption procedure was repeated three times for each initial concentration, so each experimental point on the sorption isotherm is the mean value of three separate determinations. The same procedure was used for chrysoidine sorption, with concentrations ranging from 0.04 mM to 3.2 mM at buffered pH 4 and 7. The concentration range was selected in both cases on the basis of preliminary sorption studies. Free ofloxacin and free chrysoidine in solution at equilibrium were quantitatively determined using a Varian Cary 50 UV-vis spectrophotometer equipped with a fiber optic dip probe, as previously described (Crespo-Alonso et al., 2013; Nurchi et al., 2014). The difference between initial and equilibrium molar concentrations of sorbates, C_i and C_e respectively, allowed the evaluation of sorbed substance per unitary weight of biomass, Q_i (mmol g⁻¹), according to

$$Q_i = \frac{C_i - C_e}{\text{biomass weight}} \times V_s$$

where V_s is the solution volume, expressed in mL, whereas the biomass weight measured to four digits of precision is expressed in grams.

3. Results and discussion

3.1. Sorption kinetics

Detailed kinetic experiments were performed to determine the time required to reach equilibrium. Kinetic experiments were performed on the ofloxacin/FG grape stalk system at pH 4, 7 and 9, and on the chrysoidine/FG grape stalk system at pH 4 and 7. The pH values were selected on the basis of

speciation of ofloxacin and chrysoidine (Crespo-Alonso et al., 2013; Nurchi et al., 2014) as described in Section 2.2. The resulting plots of Q vs the equilibration time are reported in Fig. 1. In the same figure the pseudo-first order fitting curves are drawn as continuous lines. When dealing with biomass a predicted model is often unable to describe correctly the kinetic behavior in the whole kinetic range, hence pseudo first-order and pseudo second-order equations are generally used (Lodeiro et al., 2006; Alberti et al., 2012; Nurchi et al., 2014).

The experimental data in Fig. 1 are, instead, completely described by a pseudo first-order kinetic model, and the pseudo first-order kinetic constants were estimated according to the equation

$$\ln(Q_{\max} - Q) = \ln Q_{\max} - kt$$

where Q_{\max} is the maximum value of Q at the reached equilibrium, k is the first order kinetic constant, and t is time in seconds (Table 1).

The kinetic profiles (Fig. 1) and the kinetic constants (Table 1) for ofloxacin show that, though the Q_{\max} values at equilibrium differ greatly, the kinetic constants at the three examined pHs are almost equivalent, leading to equilibrium achievement in about 120 min. Instead, in the case of chrysoidine, double that time is required in the sorption procedure: the sorption takes place at a slower rate, hence about 180 min are required at pH 4 and 7. Once ascertained that the required equilibration time is in the order of two and three hours for ofloxacin and chrysoidine, respectively, an overnight contact time, representing an infinite time, was used for practical reasons on both the size FG and GG fractions.

3.2. Sorption isotherms

Sorption isotherms were evaluated on grape stalk of two different sizes with the two molecules, ofloxacin at pH 4, 7 and 9 and chrysoidine at pH 4 and 7. The experimental isotherms are reported as points in Figs. 2 and 3 for ofloxacin and chrysoidine, respectively.

According to the reported results, a different behavior between FG and GG is always observed for ofloxacin, being FG characterized by higher Q_{\max} values. The sorption at pH 7 is significantly lower than those at pH 4 and pH 9. All the

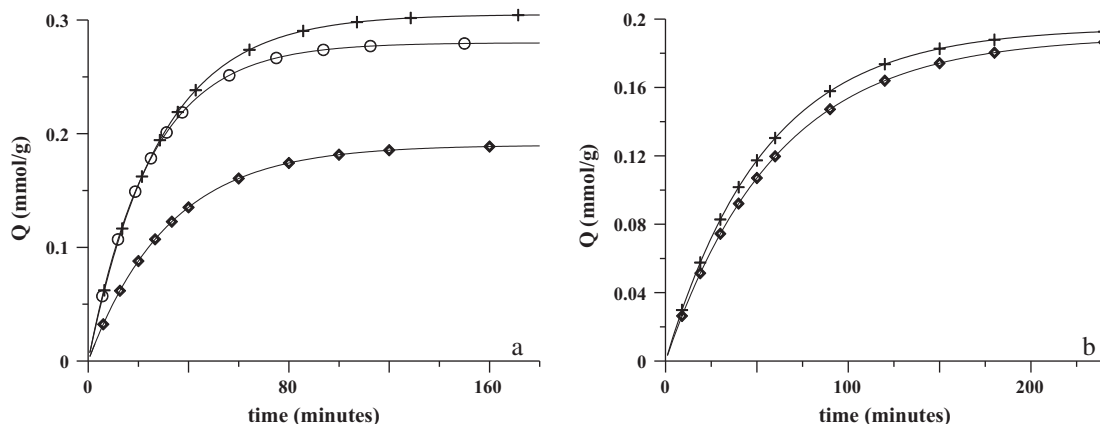


Figure 1 Kinetic behavior of FG grape stalk toward (a) ofloxacin pH 4 (+), pH 7 (◇) and pH 9 (○); (b) chrysoidine at pH 4 (+) and pH 7 (◇).

Table 1 First-order kinetic constants (s^{-1}) at different pH values for ofloxacin (FG samples) and for chrysoidine (FG samples).

pH	Ofloxacin k (s^{-1}) $\times 10^4$	Chrysoidine k (s^{-1}) $\times 10^4$
4	5.90 (3)	3.12 (1)
7	5.18 (1)	2.77 (2)
9	6.75 (4)	

six experimental isotherms are fitted by the Langmuir equilibrium model (Figs. 1–6 in Supplementary materials). The literature proposes different models for representing isotherms, from the simplest Langmuir model to increasingly complex alternatives. One corner stone of equilibrium solution studies, Occam's Razor theory, states that when a choice has to be made among different equilibrium models, which equally fit the experimental data and all of them have a realistic physical meaning, the simplest model should be preferred (Forster, 2000). Langmuir isotherm absorption model is represented by the equation

$$Q = \frac{Q_{\max} \times K \times C}{1 + K \times C}$$

where Q (mmol g^{-1}) is the amount of sorbate at equilibrium, Q_{\max} (mmol g^{-1}) the saturation capacity at a given pH, K (mM $^{-1}$) the Langmuir constant, and C (mM) the analyte

concentration at equilibrium in the solution phase. The K and Q_{\max} parameters relative to ofloxacin sorption are reported in Table 2.

These parameters allow us to make a better discussion of the previous observations. A different behavior between FG and GG is observed at all the three pH values: Q_{\max} for FG is always higher than Q_{\max} for GG, while K is almost the same (in the limits of experimental error) for FG and GG at pH 4 and 9 and higher for GG at pH 7. In particular, K values increase continuously with pH, mainly from pH 7 to 9, whereas Q_{\max} decreases (about 50%) from pH 4 to pH 7, and increases again to pH 9. The differences of Q_{\max} values between the FG and GG samples cannot be simply ascribed to a different surface area. In fact, if we assumed a spherical form, FG particles should be characterized by a mean diameter of ca. 0.4 mm, whereas GG particles of ca. 1.6 mm. This size implies a ratio of about 4 between the surface areas of FG and GG for an equal volume (or weight) of biomass. Being the experimental FG vs. GG Q_{\max} ratio only ca. 1.4, it is evident that the observed difference cannot be directly related to surface area. In the absorption of ofloxacin by cork of two different size particles we observed that the behavior of the sorption isotherms was not dependent from size at pH 4 and 7, while it was well differentiated at pH 9 (Crespo-Alonso et al., 2013). In that study it was hypothesized that the entire volume of biomass was involved in the sorption process – i.e., the cork, due to its porosity, renders its sorbing interior

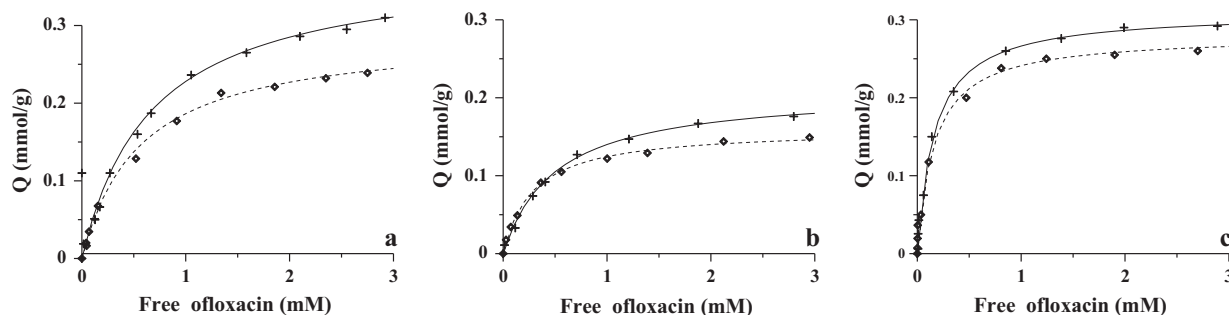


Figure 2 Amounts of sorbed ofloxacin per unitary weight of sorbent. Q is reported as a function of free ofloxacin at equilibrium: (a) FG at pH 4 (+), GG at pH 4 (◇), (b) FG at pH 7 (+), GG at pH 7 (◇), and (c) FG at pH 9 (+), GG at pH 9 (◇). The lines are the Langmuir sorption isotherms calculated with the parameters in Table 1.

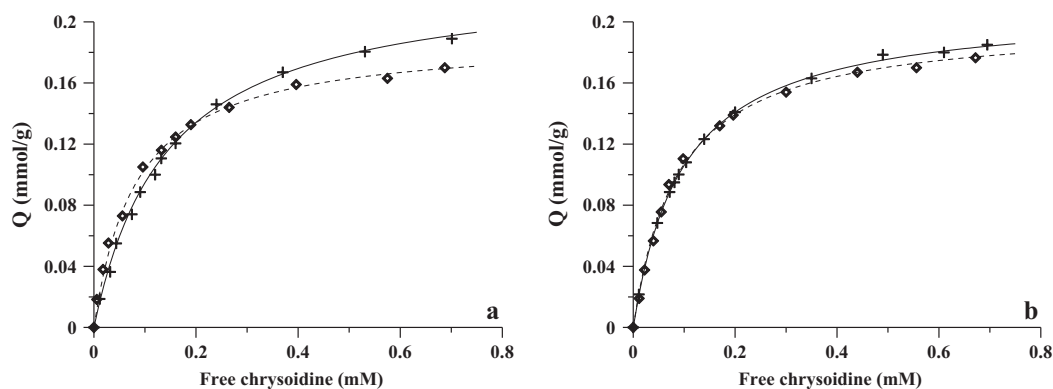


Figure 3 Amount of sorbed chrysoidine per unitary weight of sorbent. Q is reported as a function of free chrysoidine at equilibrium: (a) FG at pH 4 (+), GG at pH 4 (◇), (b) FG at pH 7 (+), GG at pH 7 (◇).

Table 2 Langmuir parameters calculated for ofloxacin sorption by two different sizes of grape stalk (FG and GG), and at pH 4, 7 and 9.

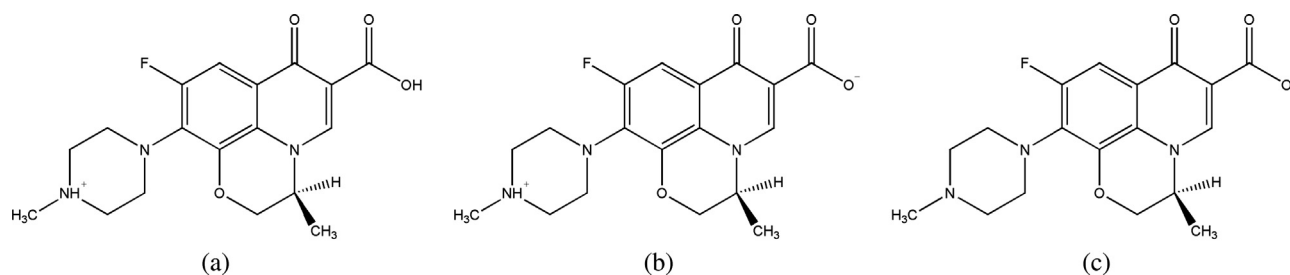
pH	Case	$K(\text{mM}^{-1})$	$Q_{\text{Max}}(\text{mmol/g})$	$Q_{\text{Max}}(\text{mg/g})$
4	FG	1.5(1)	0.38(1)	137.3
	GG	1.8(1)	0.29(1)	104.8
7	FG	2.0(1)	0.21(2)	75.9
	GG	3.5(2)	0.16(2)	57.8
9	FG	6.1(2)	0.31(2)	112.0
	GG	6.2(2)	0.28(1)	101.2

completely accessible to the sorbate molecule, like a “real sorbing sponge”. In such a situation the size of the sorbing material does not affect the number of sorbing sites. On the other hand, being the grape stalk characterized by a lower porosity than cork, the decrease of the volume of the particles causes an increase of the surface area with a concomitant increase in accessible sites. In order to explain the different pH behavior both the changes of surface charge and the speciation of ofloxacin have to be taken into consideration: the grape stalk PZC of 5.0 (Fiol and Villaescusa, 2009) implies that its surface is positively charged at pH 4 and negatively at pH 7 and 9. According to the protonation constants of ofloxacin ($\log K_1$ 8.28, $\log K_2$ = 6.00) and to the speciation plot previously reported (Crespo-Alonso et al., 2013), ofloxacin exists as a species positively charged on the piperazine nitrogen atom at pH 4, as zwitterionic form, positively charged on piperazine moiety and negatively charged on quinoline moiety, at pH 7, and as the species negatively charged on quinoline at pH 9 (see Scheme 2).

At pH 4 an electrostatic sorption mechanism can be definitely excluded, since both the sorbate and the sorbent are positively charged. On the basis of modeling studies, π - π interaction between grape stalk and paracetamol, and cork and pesticides have been proposed (Villaescusa et al., 2011; Olivella et al., 2015). A similar mechanism has to be considered in our case, acting on the aromatic quinoline moiety of oflox-

acin and the aromatic syringyl and guaiacyl groups on lignin. At pH 4 π - π interaction should be maximal since the phenolic groups of syringyl and guaiacyl are completely protonated. At pH 7 the molecule of ofloxacin is found in zwitterionic form, thus negatively charged on the carboxylic group in the quinolone moiety and positively on the piperazine nitrogen. This conformation favors the ofloxacin approach to the grape stalk surface through the positively charged part, and hinders, for electrostatic reasons, the stacking interaction, leading to a drastic decrease in ofloxacin sorption at pH 7. Instead, a different mechanism should be invoked to justify the increase of sorption parameters at pH 9. In this case it is possible to envisage the interaction of the lone-pair on piperazine nitrogen atoms with some Lewis acidic groups on the sorbent surface (Pujol et al., 2013), or with phenolic groups giving rise to hydrogen bonds (Olivella et al., 2015).

Since the protonation constant of chrysoidine is $\log K$ 5.41 (Nurchi et al., 2014), the isotherms were determined at pH 4, where the completely protonated form exists, and at pH 7, where the neutral form is present. The sorption procedure was performed on the two sizes of grape stalk, FG and GG, and the results are reported in Fig. 3 as symbols and the sorption isotherms calculated according to the Langmuir model as continuous lines. On the basis of the Langmuir parameters (Table 3) and of a visual analysis of plots in Fig. 3, some considerations can be brought forward. The Q_{max} values for FG

**Scheme 2** Ofloxacin species existing at pH 4 (a), pH 7 (b) and pH 9 (c).**Table 3** Langmuir parameters calculated for chrysoidine sorption by two different sizes of grape stalk (FG and GG).

pH	Case	$K(\text{mM}^{-1})$	$Q_{\text{Max}}(\text{mmol/g})$	$Q_{\text{Max}}(\text{mg/g})$
4	FG	9.7(3)	0.23(1)	48.8
	GG	12.0(2)	0.19(2)	40.3
7	FG	10.2(2)	0.21(2)	44.6
	GG	11.5(2)	0.20(2)	42.4

are comparable with those for GG, even if slightly higher. The K values for FG are instead lower than those for GG. In light of the previous consideration about ofloxacin, we can assume that chrysoidine, given its smaller dimensions, takes advantage of the grape stalk porosity.

The Q_{\max} calculated for chrysoidine is almost of the same order of magnitude as those calculated for ofloxacin. This similarity implies that the same coordinating sites on grape stalk are used by both the molecules, presumably the syringyl and guaiacyl groups through a π - π interaction. However, it should be noted that the higher K values denote a stronger interaction of the unsubstituted aromatic moiety of chrysoidine with the grape stalk counterparts.

4. Conclusion

The above data indicate that an absorption mechanism is mainly responsible for the grape stalk action, with a small super-imposed adsorption contribution – especially in the case of the bigger molecule ofloxacin. Our observations should be compared with the results published in the literature, taking into account that the chemical (mmol/g) instead of technical (mg/g) units is recommended to make this kind of comparison (Nurchi and Villaescusa, 2008). Unfortunately, the only results found in the literature relative to grape stalk action on organic molecules are those for paracetamol at pH 6 (Villaescusa et al., 2011). The Q_{\max} value reported in that work (~ 0.014 mmol g⁻¹) is significantly lower than those presented here for both the molecules (~ 0.2 mmol g⁻¹). Further, the time required to reach equilibrium in paracetamol case (~ 16 h) is much higher than the time measured for chrysoidine (~ 3 h) and ofloxacin (~ 2 h). Instead, our Q_{\max} values are ten times lower than that reported for paracetamol on activate carbon (~ 2 mmol g⁻¹) (Beninati et al., 2008; Ruiz et al., 2010). We can also compare the present values with those found for the same molecules with cork (Crespo-Alonso et al., 2013; Nurchi et al., 2014): both K and Q_{\max} are comparable with chrysoidine, so that no substantial technical differences between the two biomasses are found, while in the case of ofloxacin a significant increase in sorbing capacity is found passing from cork to grape stalk.

As concluding remarks, we have to suggest that whenever an emerging pollutant is present in wastewater (hospitals, intensive breeding farms or textile industry, and so on) a preliminary treatment with a suitable biomass should be performed in order to reduce the amount of toxic substances discharged into the sewer system. The short contact time for an adequate sorption, the sorption capacity and the fact that grape stalk wastes do not require preliminary treatments and, once used, can be burned under controlled condition qualify this biomass as a noteworthy candidate for organic pollutant elimination in all the wine producing countries where grape constitutes an abundant by-product. A practical engineering study has to be performed to design a scalable practical implementation.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.arabjc.2015.01.006>.

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